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THE INFLUENCE OF MOLECULAR CLUSTERS ON LUBRICATING FILM FORMATION

Antoni Jankowski[1(*)], Miroslaw Kowalski[1], Andrzej Kulczycki[1], Wojciech Dzięgielewski[1], Jarosław Kałużny[2], Jerzy Merkisz[2]
[1]Air Force Institute of Technology, Poland; [2]Poznan University of Technology, Poland
[(*)]*Email:* antoni.jankowski@itwl.pl

ABSTRACT

The paper presents the results of investigations focused on the role of the environment (base lubricant) of lubricating additives on their effectiveness in lubricating film formation. The proposed novel mechanism of lubricating additives takes into account the role of molecular clusters in electrical conductivity regulation. The results of experimental investigations, shown in the paper, initially confirm the proposed mechanism of lubricating film formation. The presented test results confirmed that the formation of a thick lubricating film by the lubricant is possible only if the oil composition contains an "energy carrier"

Keywords: lubricant, lubrication, lubrication additives, lubricating film formation, molecular cluster.

INTRODUCTION

Previous concepts of the mechanism of lubricating film formation under boundary conditions can be simplified down to the interaction between additive molecules and surface of machine element being lubricated. The above-mentioned mechanisms have been developed for many decades as well as widely described in many publications regarding tribochemistry. This mechanism does not explain many experimental data, including the influence of base fuel or oil (without additives) on the ability of lubricating additives to form a lubricating film.

To obtain the appropriate lubricating properties of substances that perform the function of lubricants (fuels, lubricating oils) among others, various types of lubricity additives are introduced (Kałużny, 2017). They are attributed the ability to reduce the wear of lubricated machine elements and reduce the friction resistance. Lubricated machine parts are subjected to various driving forces (pressure force, slip speed). Lubricating additives selected experimentally for various parameter ranges differ in their chemical structure. The additives for fuels, mainly for diesel and turbine engine fuel, are organic acids or their derivatives (Jankowski, Kowalski, 2015). Additives for lubricating oils, including motor oils, are most often compounds from the group of zinc dithiophosphates. The influence of the chemical structure of the additive on the efficiency of its operation is the subject of many studies. However, experience shows that the efficiency of lubricating additives is also dependent on the properties of the lubricant base. The dependence of the effectiveness of the lubricity additive, on the properties of the base lubricant (base oil, fuel) to which it is introduced, is one of the significant problems in the selection of lubricating additives packages for fuels and lubricating oils. The mechanisms proposed so far, for the formation of the lubricating layer by the lubricating additives molecules allow, however, to only taking into account the role of the lubricant base in this process to a negligible extent (Gosvami, 2015; Spikes, 2004).

The authors have proposed the novel concept of the mechanism of lubricating film formation previously. The novel concept is the result of mathematical model of tribochemical processes, described previously (Kulczycki, 1985; Kajdas, 2008).

$$\alpha_i = (L - L_0) / A \exp[-E_a/(RT + \varepsilon)] [(e_0) \cos (k_2 L + k_3)] t \quad (1)$$

where: α_i - coefficient of lubricating additives reactivity; L - mechanical work that should be done in a tribological system to reach the critical condition, e.g. seizure; L_0 - mechanical work that should be done in a reference system to reach the critical condition, e.g. seizure; T - temperature of liquid phase where the reaction takes place, e.g. boundary layer; ε – energy introduced into the reaction space, other than heat (RT); e_0 - energy stream emitted from the surface of the solid body (catalyst) as low-energy electrons (perpendicular to solid surface); A, k_2, k_3 - constant values; t - time.

The above mathematical model refers to this group of lubricity additives, which in the tribological process undergo chemical reactions, and the efficiency of their operation is related to the rate at which these reactions take place. The mathematical quantities appearing in the above-mentioned model are associated with various forms of energy supplied to the reagents (including lubricity additives). RT reflects the heat brought into the reaction space, ε- other forms of energy, mainly the energy of electrons and/or photons emitted by the lubricated surface. The results of previous studies (Kajdas, 2017; Kulczycki, 2017; Kulczycki 2014; Kulczycki, 2016) linking the equation (1) with experimental data allowed proposing the following mechanism:

- in the tribological process - in the process of lubrication the energy flows in two directions: from the lubricated surfaces to the lubricating film and from the lubricating film to the lubricated surfaces
- the dominance of one of these energy flow directions determines the location of the chemical reactions which the lubricity additives are subjected to and, consequently, the type of protective layer produced by these additives
- in the case where energy flow to the lubricated surface is dominant the chemical reactions of the lubricity additive are moved to the surface of the solid; the protective layer is formed from the reaction products of the lubricity additive in the form of a permanent deposit on the lubricated surface
- in the case where energy flow from the lubricated surface is dominant, the location of chemical reactions of the lubricity additive can be pushed away from the lubricated surface; chemical reactions of the lubricity additive allow the formation of a lubricating film of considerable thickness.

For efficient energy transfer from the lubricated surface to the distant parts of the film, appropriate molecular structures characterized by the ability to conduct energy are necessary. Such structures may be molecular clusters, whose occurrence in fuels and lubricating oils is more and more often presented in the literature (Manil, 2003; Gatchell, Chen, 2014). Clusters, ordered molecular structures, are characterized by properties other than those of molecules outside the cluster structure. One of the characteristics of clusters is the ability to accumulate energy and the ability to conduct energy, through paths determined by the cluster structure.

In the proposed novel concept of the lubricating film formation mechanism by the lubricant containing a lubricity additive, the role of the molecular structures able to accumulate and conduct energy was taken into account, Figure 1. It was assumed that molecular ordered structures play an important role in creating the lubricating film. Due to their arrangement, these structures are difficult to remove from the space in which friction occurs. When friction occurs, they absorb energy from the surface of the lubricated elements and can discharge it outside the friction zone, where it is dispersed into the environment. Depending on the friction conditions (pressure, slip speed); the process can be disturbed when the amount of cumulated energy leads to the destruction of the ordered cluster structure. In these conditions, the lubricating film cannot be formed or interrupted. The cumulative energy in molecular clusters can be taken over by the lubricant additive particles. The energy taken over allows initiating the endothermic chemical reaction of the additive, thanks to which the cumulated energy in the clusters is transferred to the reaction products of the lubricity additive. These endothermic reactions of lubricity additives may be reversible, but the inverse, exothermic reaction takes place out of the friction zone, and the generated energy may be dispersed into the surroundings more easily. The proposed mechanism is schematically shown in Figure 2.

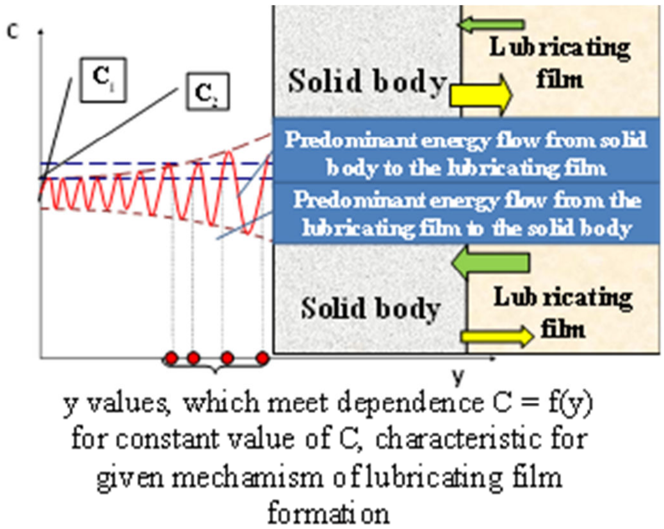


Fig. 1 - The relation C = A exp[-E_a/(RT + ε)] [(e_0) cos (k_2L + k_3)]t from the value of parameter y, which was assumed as a variable that determines the energy response value of the tribological system to external driving force (L = f(y))

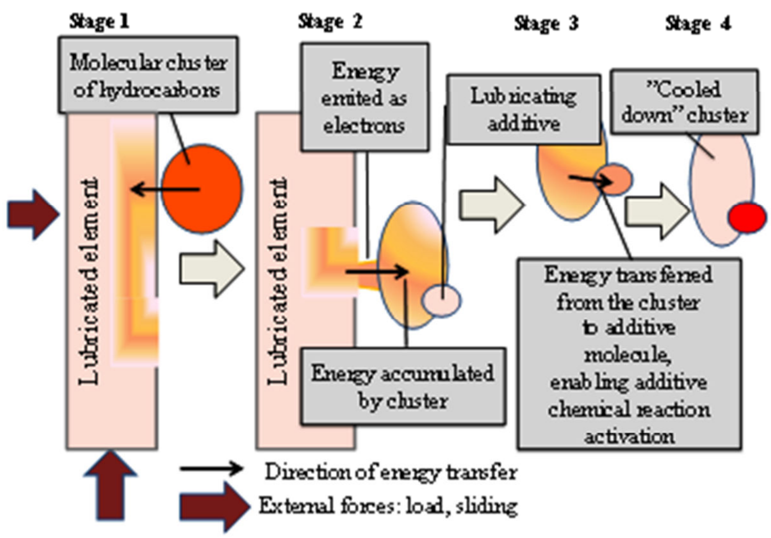


Fig. 2 - The mechanism of lubricity additives impact in the AW area, postulated based on previous test results

The aim of the research presented in this article is the experimental verification of the proposed action mechanism of the lubricity additives and the role of molecular structures that conduct energy in the formation of a lubricating film.

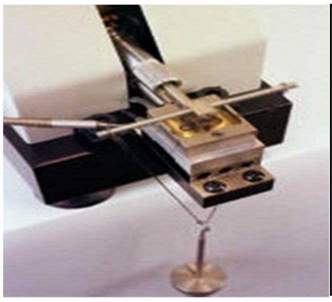
The following hypothesis has been formulated: (a) lubricating additives undergo chemical reactions in the friction process, creating a thin layer of durable deposits on the metal surface; deposits partially reduce wear, but they are not the lubricating film; (b) lubricating film is formed by additives, which undergo chemical reaction inside the film; the kinetics of this reaction depends on energy transfer from the metal surface to the molecules of the additive (located inside the film); (c) trigonometric part of eq. (1) shows the preferred pathway of energy transfer across the film.

RESEARCH METHODOLOGY

The tribological test on the HFRR (High Frequency Reciprocating Test Rig) apparatus was selected for the verification of the postulated mechanism. This test was chosen due to (Dzięgielewski, 2015):

- large accumulation of energy on a small surface area,
- a relatively low value of mechanical forcing − low load,
- possibility of continuous measurement of the friction coefficient and the thickness of the lubricating film during the test.

The test was conducted in standard conditions for fuels, i.e. according to PN-EN ISO 12 156, according to the procedure described in the PN-ISO 12156 modified for the purposes of this work. The HFRR apparatus is shown in Figure 3.



The test conditions are as follows:

- Test duration - 75 min
- Frequency of upper ball vibration - 50 Hz
- Load - 200 g or 500 g
- Temperature of tested fuel at the beginning of the test - 60 ^{0}C

Fig. 3 - HFRR apparatus-friction node and test conditions

A synthetic oil base PAO 6 was selected for the tests. PAO base oils are a mixture of isoparaffin hydrocarbons. They do not contain ring hydrocarbons, including aromatic hydrocarbons. Therefore, they do not contain ingredients predisposed to creating ordered molecular structures. The basic properties of the PAO 6 oil are shown in Table 1.

Table 1 - PAO6 oil properties

Properties	Unit of measurement	Value	Method
Specific gravity at 15.6 °C	g/cm^3	0.827	ASTM D4052
Kinematic viscosity at **100 °C** **40 °C** **−40 °C**	mm^2/s	5.8 31.0 7800	ASTM D445
Viscosity Index		138	ASTM D2270

In order to verify the hypotheses presented above, lubricating oils were prepared with the composition as listed below:

1. PAO6
2. PAO6 + 1.5%(m/m) ZDDP
3. PAO6 + 6 ppm ASA
4. PAO6 + 1.5% (m/m) ZDDP + 6 ppm ASA
5. Commercial engine oil SAE 5W-30 VW-norm 504.00/507.00

To prepare these oils the following additives were added to PAO6:

- a commercial lubricity additive - zinc dithiophosphate with primary alkyl groups (ZDDP)
- a commercial additive (ASA) dedicated fuels for turbine aircraft engines in order to increase their electrical conductivity.

Table 2 - The properties of Zn dithiophosphate (ZDDP)

Properties	Unit of measurement	Value	Method
Density (25°C)	kg/m^3	1160	ASTM D1298
Viscosity (40°C)	mm^2/s	150	ASTM D445
Zn content	% weight	9.0	-
P content	% weight	8.5	-
S content	% weight	16.5	-

The ASA additive is a composition consisting of a C/H/O/S polymer, polyamine and an R-SO3H stabilizer. The chemical structure of the ASA additive indicates that its components can form ordered molecular structures, so that even at very low concentrations (3 ppm) it can significantly increase the electrical conductivity of the lubricant. The special properties of molecular clusters indicate that they can be responsible for energy transfer from metal surface to the additive molecules inside the film. It was assumed that ASA could play the same role, when it is added to PAO6 base oil.

All of the test oils were tested on the HFRR apparatus. During the tests, the coefficient of friction and the thickness of the lubricating film were measured. After the tests, the wear track was measured on the test ball, and the test plates were analysed for the topography of the wear track and the EDS analysis of the wear track.

RESULTS

Table 3 and Figures 4, 5 and 6 present the results of the HFRR apparatus tests for the tested oils.

Table 3 - HFRR results for the tested lubricants

Tested oil	Wear scare corrected [μm]	Average film thickness [% acc. to HFRR method]	Average friction coefficient
PAO	422	1.4600	0.1954
PAO6 + 6 ppm ASA	380	1.0778	0.1942
PAO6 + 1.5%(m/m) ZDDP	285	5.8978	0.1287
PAO6 + 1.5% ZDDP + 6 ppm ASA	200	70.0666	0.1294
Commercial engine oil SAE 5W-30 VW-norm 504.00/507.00	147	80.5178	0.04726

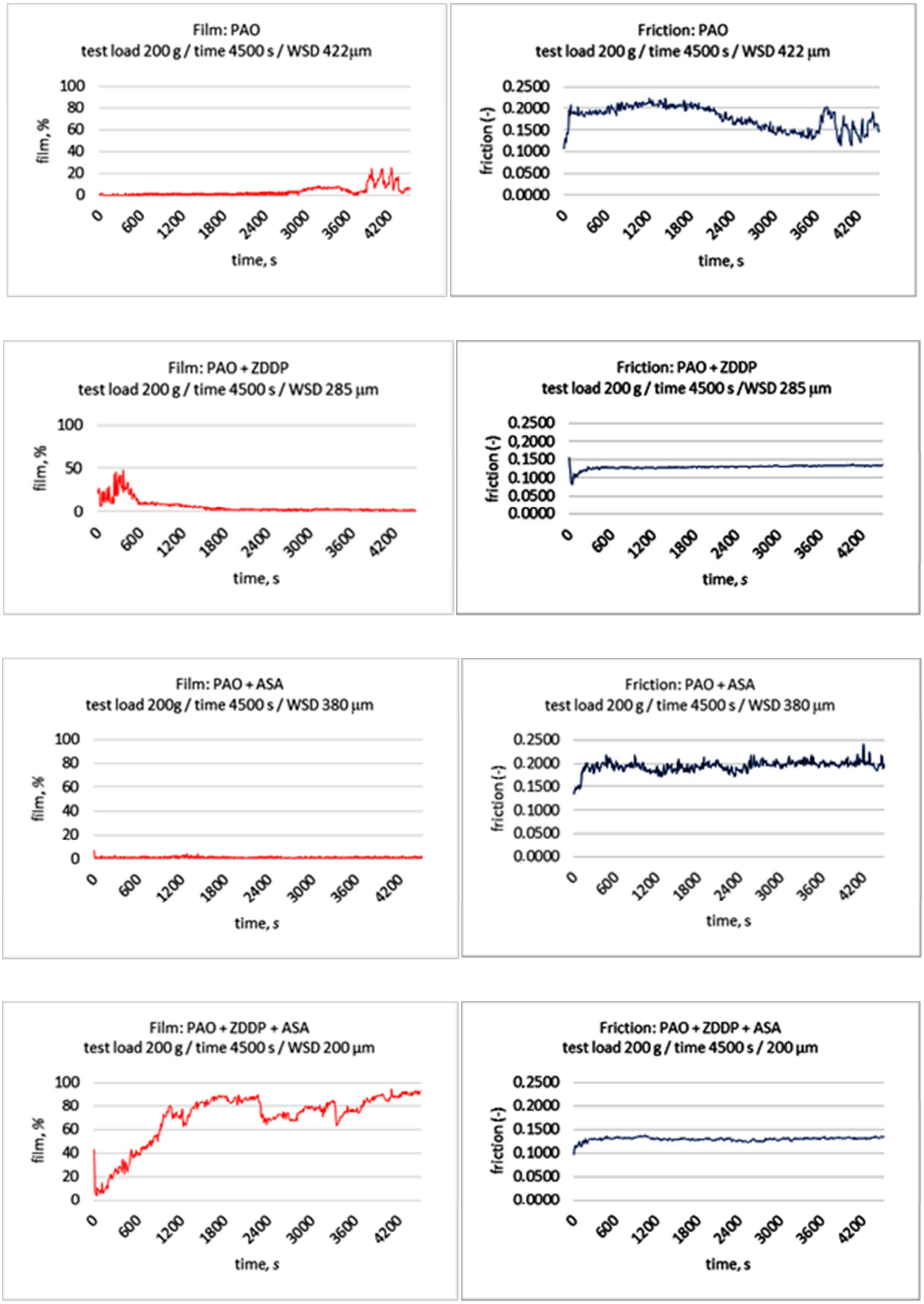


Fig. 4 - The changes in the thickness of the lubricating film for PAO6-based tested mixtures in the HFRR test

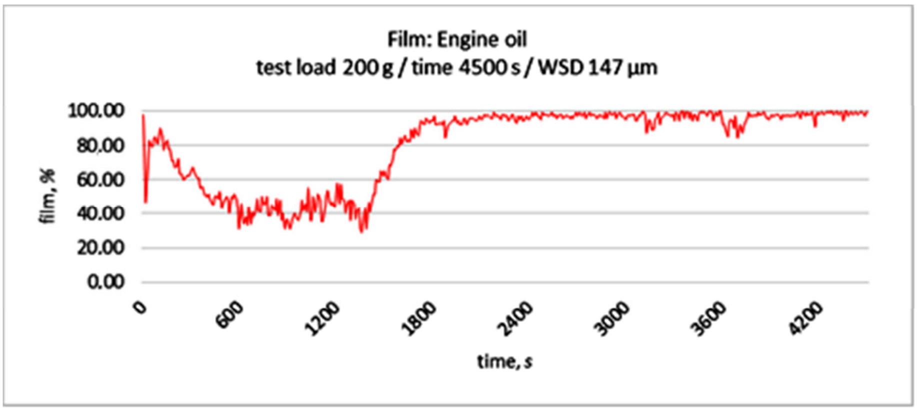
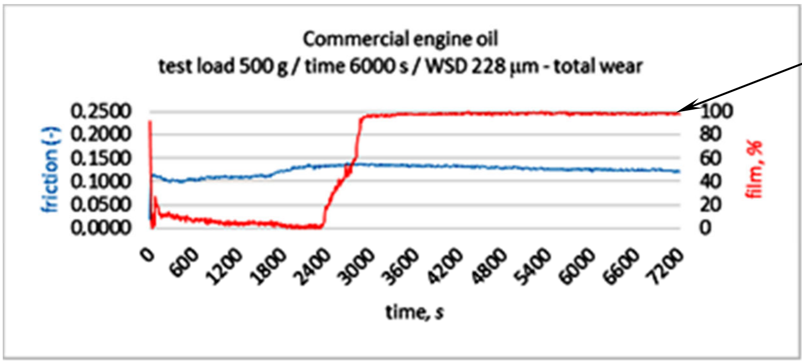
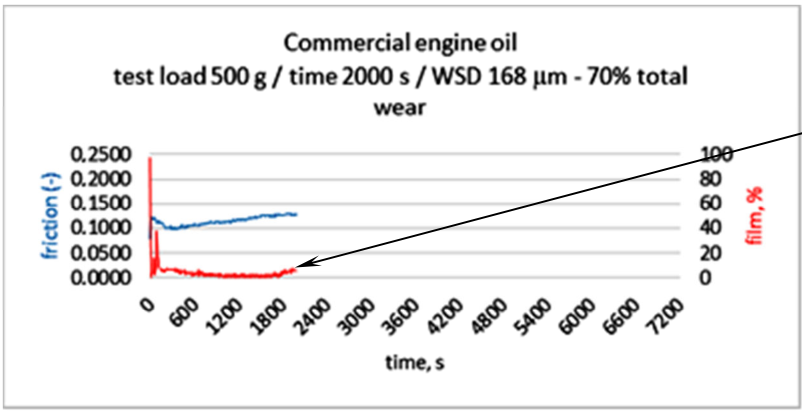


Fig. 5 - The changes in the thickness of lubricating film for engine oil in the HFRR test

In addition, HFRR tests of commercial engine oil were carried out at a higher load of 500g. The test was done for standard time duration of 75 minutes and then repeated (using a new ball, plate and oil sample) for about 20 minutes, i.e. in less time than required to form a lubricating film. After this time, the wear of the test ball was measured and the EDS analysis of the wear track on the test plate was carried out. The results presented in Figure 6 indicates that in the period before the creation of a lubricating film on the lubricated surface, ZDDP created a deposit layer consisting of sulphur, phosphorus and zinc compounds.



Element	Line	Wt.%	At%
O	KA1	2.16	6.85
P	KA1	2.83	4.63
S	KA1	3.37	5.32
Zn	LA1	10.48	8.12
Total		100.00	100.00



Element	Line	Wt.%	At%
O	KA1	2.29	7.16
P	KA1	2.63	4.25
S	KA1	4.59	7.17
Zn	LA1	8.37	6.69

Fig. 6 - Results of the commercial engine oil in the HFRR test at a load of 500 g. Blue line-coefficient of friction

The EDS results presented in Figure 6 indicate that the elemental composition of the deposit did not change significantly after creating a thick lubricating film.

FRICTION TRACK TOPOGRAPHY

Figure 7 shows the topography of abrasion tracks on plates after the HFRR test. The topography of wear tracks is similar in all studied cases. Near the turning points of the HFRR apparatus (the smallest slip speed), clear depressions are visible, while in the central part of the track (the highest slip speed) a pronounced bulge is observed. Clear accumulation of the material at the edges of the wear tracks was observed. Depending on the composition of the tested lubricant, the width of the wear track is different and corresponds to the width of the wear track on the ball. Figure 7 presents the example topography of wear marks of plates lubricated with pure PAO 6 oil and PAO 6 oil containing the additives of ZDDP and ASA.

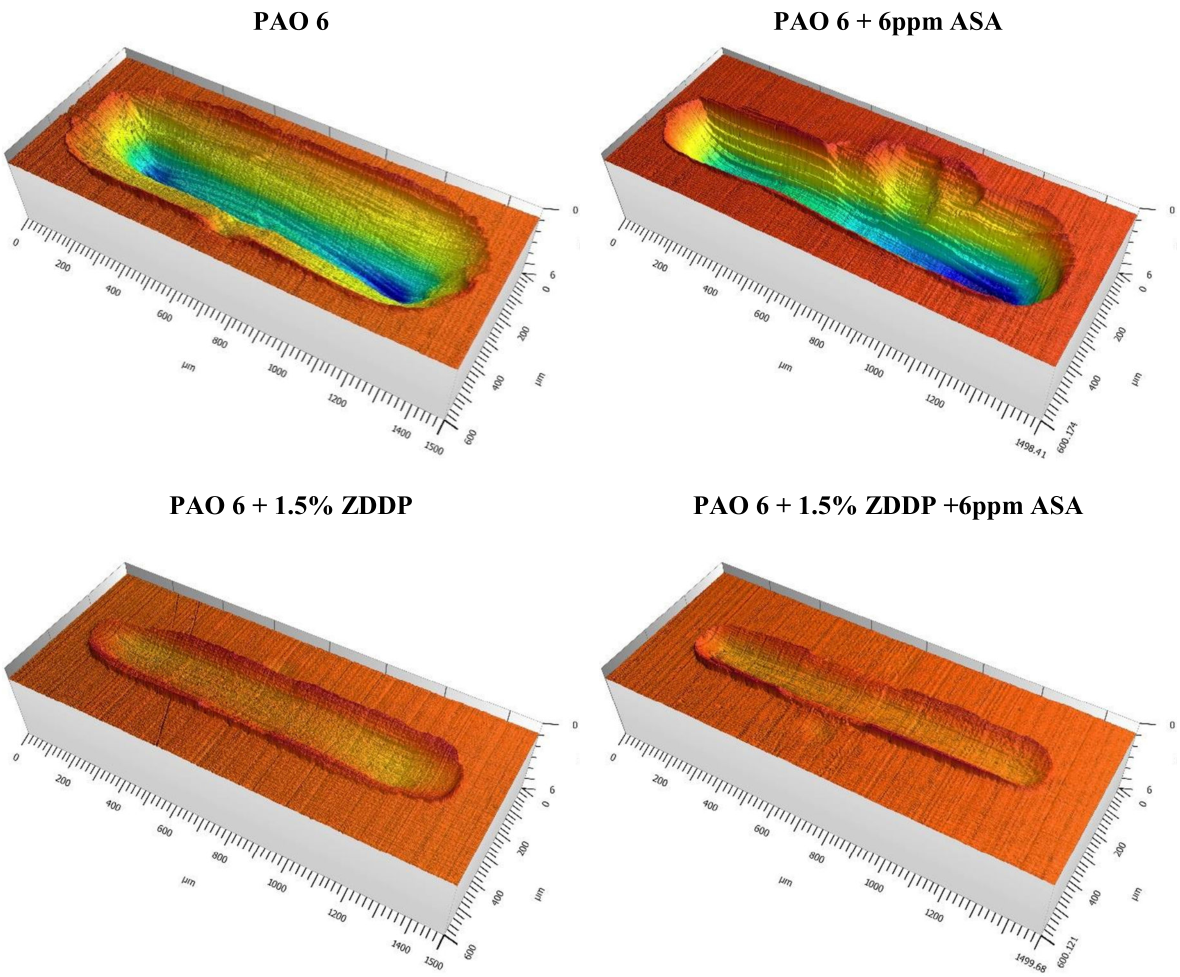


Fig. 7 - Impact of the tested PAO 6 additives on the wear track on the HFRR plate, for the comparison all 3D topography pictures are presented at the same magnification

The anti-wear function of ZDDP can be clearly interfered from Figure 7, when compared to the results obtained for the base oil without additives or to the same oil enriched only with ASA. This result could be clearly predicted since ASA is not an AW additive. At the same time the addition of ASA to ZDDP containing oil results in clearly reduced wear scar documenting the synergistic effect of ZDDP and ASA in the anti-wear function.

EDS ANALYSIS

EDS mapping was performed for all plates in the area covering about 1/3 of the length of the friction track. There is always an extreme part of the friction path together with a fragment of the surface not subject to friction in the EDS analysis field of view. In order to limit the depth of the forcing zone, the tests were carried out at an acceleration voltage of 8 kV. This allowed the analysis of the chemical composition from a very small depth. The mapping results are shown in Figure 8. Similar results were observed by Qu (Qu, 2015).

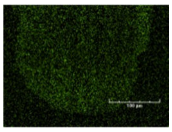
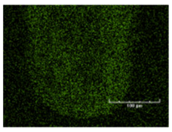
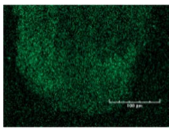
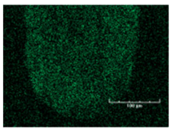
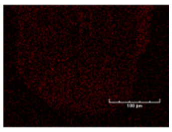
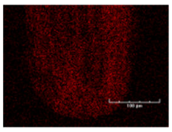
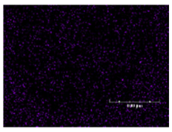
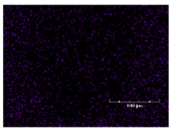
	PAO 6 + ZDDP	**PAO 6 + ZDDP + ASA**
P		
S		
Zn		
Fe		

Fig. 8 - EDS method test results for the plate surfaces wear tracks after the HFRR test for the PAO6 + ASA + ZDDP mixture

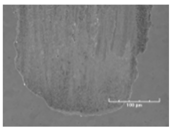
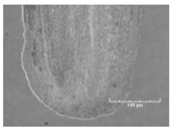
	PAO 6 + ZDDP	**PAO 6 + ZDDP + ASA**
SEM		

Fig. 9 - SEM pictures - comparison for the plates lubricated with ZDDP containing PAO 6 oil and the same mixture enriched with ASA; SE, 8 kV

EDS studies indicate that ZDDP creates permanent deposits, which are chemical reaction products of zinc dithiophosphate.

DISCUSSION

According to the most common interpretation in the literature, additives from the ZDDP group are adsorbed on the surface of the lubricated elements, followed by chemical reactions, creating stable products - deposits. These deposits are attributed to counteracting the material wear of the friction components and counteracting scuffing that results from breaking the lubricating film. The question then arises whether these deposits can be equated with the concept of a lubricating film, or whether they replace a lubricating film in cases where the lubricating film is broken. Views on this subject are varied. Most friction tests boil down to the examination of the conditions in which the lubricating film is broken (e.g. tests on a four-ball device). Published experimental data do not contribute to the development of a coherent concept of lubricating film and the mechanism of its creation with the participation of lubricity additives.

The results of the HFRR test presented above, with low forcing values (load, slip speed) in relation to the friction tests typical for lubricating oils, indicated that in HFRR test conditions, the lubricating film does not exist from the beginning, but can be created after a certain time. It has been observed that the condition for creating a film of appropriate thickness is the presence of not only the ZDDP additive, but also the addition of ASA increasing the electrical conductivity. Even a fully formulated engine oil, consisting of a synthetic base and a package of enhancers, is capable of forming a thick lubricating film only after a certain duration of the test. As shown in the results presented in Table 2, the creation of a lubricant film of considerable thickness significantly reduces wear. In order to analyse the impact of ZDDP and ASA additives on the course of the HFRR wear process and the presence of stable chemical reaction products of the ZDDP additive on the lubricated surface, wear marks on the test plates topography was checked for signs of wear along with the EDS wear tracks method.

CONCLUSIONS

The presented test results confirmed that the formation of a thick lubricating film by the lubricant is possible only if the oil composition contains an "energy carrier" - in this case an ASA additive, increasing the electrical conductivity. Analysis of the obtained research results leads to the conclusion that the addition of ASA, which can be associated with an ordered molecular structure, is responsible for transporting energy from the surface of the lubricated element into the lubricating film (Figure 10). This conclusion is consistent with the mechanism of creating a thick lubricating film postulated above.

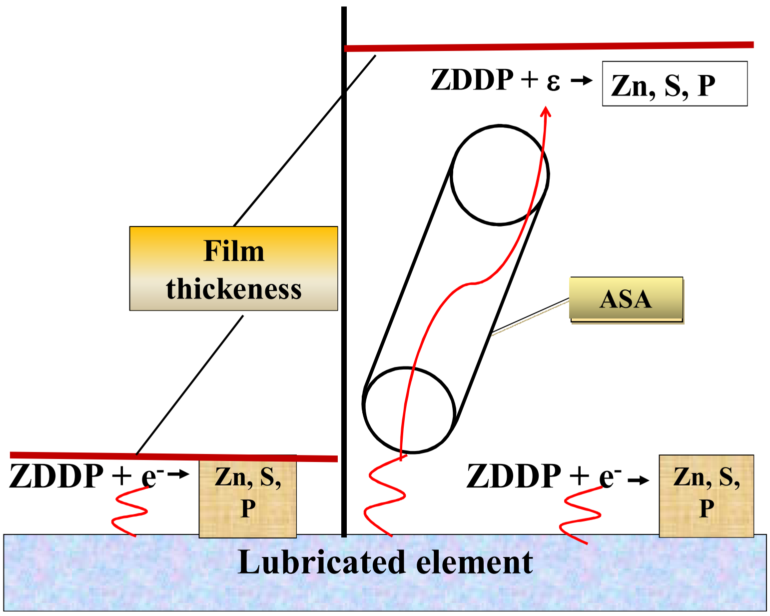


Fig. 10 - The concept of the ordered molecular structures role in the formation of a thick lubricating film

The research results presented in this article are consistent with those postulated in earlier publications (Kajdas, 2017; Kulczycki, 2017) regarding the mechanism of catalytic effect of lubricated surfaces on chemical reactions of lubricity additives, e.g. ZDDP and allow to propose a mechanism for creating a thick lubricating film under boundary friction conditions. This mechanism was based on the role of ordered molecular structures - molecular clusters, in the transport of energy from the lubricated surface into the lubricant film. As a result, ZDDP molecules present in the lubrication film receive the energy necessary to initiate endothermic chemical reactions at a considerable distance from the lubricated surface. The endothermic reactions of ZDDP in the volume of the lubricating film determine its durability.

The proposed mechanism of creating a lubricating film using ZDDP type additives and the role of ordered molecular structures in this process requires further verification through research.

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